

TITLE

## DIVALENT EUROPIUM-CONTAINING COMPOSITIONS

This application claims the benefit of U.S. Provisional Application No. 60/427,407, filed November 19, 2002, which is incorporated in its entirety as a part hereof for all purposes.

FIELD OF THE INVENTION

This invention relates to compositions of the formula  $\text{EuCu}_3\text{M}_4\text{O}_{12}$  wherein M is selected from the group consisting of Ge, Ti, and Sn, and mixtures thereof.

BACKGROUND OF THE INVENTION

The use of dielectric materials to increase capacitance is well known and long-used. In the past, capacitor dielectrics have fallen into two categories. Dielectrics in the first category have a relatively temperature-independent dielectric constant but the value of the dielectric constant is low, e.g., 5-10. Materials such as electrical porcelain and mica fall in this category. Dielectrics in the second category have a high dielectric constant, e.g., 1000 or more, but they are quite frequency dependent. An example is barium titanate,  $\text{BaTiO}_3$ .

Since capacitance is proportional to dielectric constant, high dielectric constant materials are desired. In order to perform acceptably in electronic circuits, a dielectric must have a dielectric constant that exhibits minimal frequency dependence. It is also desirable that the loss or dissipation factor of a dielectric be as small as possible.

Japanese Patent 2,528,117 B2 discloses superconducting materials of the formula  $(\text{M}^1)_x (\text{M}^2)_y (\text{M}^3)_z \text{O}_w$ , wherein

$\text{M}^1$  is B, Al, Ga, In, Tl, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu;  
 $\text{M}^2$  is BE, Mg, CA, Sr, Ba, Ra, Sn or Pb;  
 $\text{M}^3$  is Cu; and  
 x, y, z and w represents the molar ratio of the corresponding constituent elements.

It has been found, however, that other Europium-containing compositions function well as dielectrics.

#### SUMMARY OF THE INVENTION

This invention provides compositions of the  
5 formula  $\text{EuCu}_3\text{M}_4\text{O}_{12}$  wherein M is selected from the group consisting of Ge, Ti, and Sn, and mixtures thereof. The compositions have high dielectric constant and low loss over a frequency range of from 1 kHz to 1 MHz, and are especially useful as a capacitor in electronic  
10 devices such as phase shifters, matching networks, oscillators, filters, resonators, and antennas comprising interdigital and trilayer capacitors, coplanar waveguides and microstrips. The invention also includes a capacitor made from such a composition,  
15 an electronic device made from such a capacitor, and the use of such a composition to make a capacitor.

#### DETAILED DESCRIPTION

The compositions of this invention may be described as  $\text{EuCu}_3\text{M}_4\text{O}_{12}$  wherein M is selected from the  
20 group consisting of Ge, Ti, and Sn, and mixtures thereof. These compositions have dielectric properties that provide advantages in electronic devices requiring a high dielectric constant with minimal frequency dependence and low loss.

25 The compositions of this invention can be synthesized by the following procedure. Appropriate amounts of the starting oxides  $\text{EuO}$ ,  $\text{CuO}$  and  $\text{TiO}_2$  or  $\text{SnO}_2$  or  $\text{GeO}_2$  are weighed according to the stoichiometric ratios and mixed thoroughly in an agate  
30 mortar. The gram amounts of the starting materials used in representative examples are shown in Table 1. The mixed powder of starting materials is calcined at about  $700^\circ\text{C}$  for about 12 hours in an argon atmosphere. The powder is reground and loaded in a gold capsule and  
35 heated at about  $1000^\circ\text{C}$  for about 1 hour under about 60 kbar pressure in a tetrahedral anvil press. In both the steps, the rate at which the temperature ramps up is about  $200^\circ\text{C}/\text{hour}$  from room temperature, and the

cooling rate is about 150°C/hour from the reaction temperature to room temperature, i.e., about 20°C.

The compositions of this invention are single phase materials, and crystallize in a cubic perovskite-related  $Im\bar{3}$  structure.

Dielectric measurements can be carried out on disk samples of the compositions of this invention. The faces of a disk-shaped sample are polished with a fine-grit sand or emery paper. Silver paint electrodes are applied on the faces and dried at about 70-100°C. Capacitance and dielectric loss measurements can be performed by the two-terminal method using Hewlett-Packard 4275A and 4284A LCR bridges at a temperature of about 25°C over a frequency range of from about 1 kHz to about 1 MHz. The capacitance (C) and the dissipation factor are read directly from the bridge. The dielectric constant (K) is calculated from the measured capacitance (C) in picofarads from the following relationship:

$$K = (100 C t) / (8.854 A),$$
 where t is thickness of the disk shaped sample in cm and A is the area of the electrode in  $cm^2$ .

The advantageous effects of this invention are demonstrated by a series of examples, as described below. The embodiments of the invention on which the examples are based are illustrative only, and do not limit the scope of the invention.

Examples 1-3. The compositions  $EuCu_3M_4O_{12}$ , wherein M is Ge, Ti and/or Sn, are made by using the following procedure. For each example, appropriate amounts of the starting oxides EuO, CuO and  $TiO_2$  or  $SnO_2$  or  $GeO_2$  are weighed according to the stoichiometric ratios and mixed thoroughly in an agate mortar. The gram amounts of the starting materials used are shown in Table 1.

Table 1

Ex.	Composition		CuO	EuO
1	$\text{EuCu}_3\text{Ge}_4\text{O}_{12}$	1.5214 ( $\text{GeO}_2$ )	0.8678	0.6108
3	$\text{EuCu}_3\text{Ti}_4\text{O}_{12}$	1.3201 ( $\text{TiO}_2$ )	0.9859	0.6940
4	$\text{EuCu}_3\text{Sn}_4\text{O}_{12}$	1.7916 ( $\text{SnO}_2$ )	0.7092	0.4992

The mixed powder of starting materials is calcined at about 700°C for about 12 hours in argon atmosphere.

- 5 The powder is reground and loaded in a gold capsule and heated at about 1000°C for about 1 hour under about 60 kbar pressure in a tetrahedral anvil press. In both the steps, the rate at which the temperature ramps up is about 200°C/hour from room temperature, and the  
10 cooling rate is about 150°C/hour from the reaction temperature to room temperature, i.e., about 20°C.

X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer. The data showed all samples crystallized in a cubic perovskite-related  
15  $Im\bar{3}$  structure. The measured lattice parameters are listed in Table 2.

Table 2.

Ex.	Composition	Lattice Parameter (nm)
1	$\text{EuCu}_3\text{Ge}_4\text{O}_{12}$	0.7221(1)
2	$\text{EuCu}_3\text{Ti}_4\text{O}_{12}$	0.7429(1)
3	$\text{EuCu}_3\text{Sn}_4\text{O}_{12}$	0.7612(1)

- 20 The disk shaped samples (3mm diameter and 2mm thick) are polished to produce flat uniform surfaces and electroded with silver paint. The painted samples are dried at about 70-100°C overnight. Capacitance and loss tangent measurements are made at room temperature  
25 using a HP-4284A LCR meter over a frequency range of from about 1 kHz to about 1 MHz. The dielectric constants are high and the loss factors are low.

Variations of dielectric constant (K) and loss factor (Tan  $\delta$ ) over a range of frequency from about  $10^3$  Hz to about  $10^6$  Hz, measured at about 25°C for the samples of Examples 1-3, are shown in Table 3. The dielectric constants and loss factors have minimal frequency dependence over 3 orders of magnitude change in frequency.

Table 3.

Ex.	Composition	$10^3$ Hz		$10^4$ Hz		$10^5$ Hz		$10^6$ Hz	
		K	Tan $\delta$	K	Tan $\delta$	K	Tan $\delta$	K	Tan $\delta$
1	EuCu <sub>3</sub> Ge <sub>4</sub> O <sub>12</sub>	112	0.032	104	0.028	99	0.035	95	0.032
2	EuCu <sub>3</sub> Ti <sub>4</sub> O <sub>12</sub>	1340	0.095	1326	0.074	1293	0.065	1084	0.071
3	EuCu <sub>3</sub> Sn <sub>4</sub> O <sub>12</sub>	465	0.081	454	0.079	439	0.067	433	0.063

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